Characterization of materials using an ultraviolet radiometric beamline at SURF III

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Abstract. The completion of the upgrade of the synchrotron facilities at the National Institute of Standards and Technology (NIST) has yielded a better characterized broadband source of ultraviolet (UV) radiation at the Synchrotron Ultraviolet Radiation Facility (SURF III). A cryogenic-radiometer-based facility that uses the monochromatized radiation from SURF III has been established on beamline 4 (BL-4) to characterize detectors and optical materials in the wavelength range 125 nm to 325 nm. This upgraded cryogenic radiometry facility will be used to measure the spectral responsivity of detectors in the UV with a relative standard uncertainty of less than 10^{-2}. To demonstrate the capability of BL-4, we have performed a transmittance measurement of calcium fluoride (CaF_2). Accurate transmittance measurements of optical materials in the UV are urgently needed to evaluate which materials are the best choices for use in making lenses for UV lithography. A study of CaF_2 in spectral transmittance, surface scattering, and surface absorption is presented.

1. Introduction

The Synchrotron Ultraviolet Radiation Facility (SURF) at the NIST provides radiation with continuous spectral distribution from the infrared to soft X-ray. In recent years, X-ray and UV radiometry have become important applications for synchrotron radiation facilities [1-4]. SURF is ideal for UV radiometry because of the relatively low electron-beam energy (up to 400 MeV). In addition, the circular electron-beam orbit makes SURF a calculable source that can be used as a national standard light source. To further improve SURF accuracy for source-based radiometry, the recently completed upgrade of SURF III reduces the variation of the magnetic field along the electron-beam orbit to a few parts in 10^4 [2]. The performance of the facility as a light source is therefore more accurately characterized.

A major advance in UV radiometry at SURF is the construction of beamline 4 (BL-4) during the last few months of SURF II [3]. The BL-4 facility combines synchrotron radiation with cryogenic radiometry for a variety of applications in the wavelength range 120 nm to 325 nm, including detector calibration, detector damage studies, and optical material characterization [4]. On the completion of SURF III, BL-4 was reconnected to the facility and commissioned for UV radiometry. Among the first work at BL-4, we studied the optical properties of CaF_2 in the UV. This study is part of a NIST programme for optical materials and detector characterization in the UV, mainly motivated by 193 nm and 157 nm lithography where the accurate characterization of optical materials in absorption and index of refraction is essential for stepper-optics design at these wavelengths. This paper presents results on the transmission and absorption of two CaF_2 samples with thicknesses of 2 mm and 20 mm.

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2. Experimental set-up

A detailed description of BL-4 is presented elsewhere [3, 4]. The monochromatized radiation from SURF III has a 2 nm bandwidth and a 2 mm by 2 mm beam size. An IRD AXUV-100G Si photodiode monitors the radiation entering the detector box by means of a CaF_2 beam splitter. The samples are placed in a vacuum detector box in which are housed two in-vacuum translation stages capable of linear motion in the plane perpendicular to the direction of the incident radiation. The samples are high-grade 2 mm and 20 mm thick CaF_2 windows. One or more IRD AXUV-100G Si photodiodes are also in the detector box. The placement of the samples and detectors in the detector box can easily be arranged for a variety of measurements of sample transmittance, reflectance, and scattering. Typical operating pressure of the detector box was about 10^{-6} kPa.

Care was taken to ensure that the reflected light from the detector surface did not interreflect between optical elements and cause systematic error for the detector signal. In most cases, the detectors are tilted to

a small angle from normal incidence and the reflected light is directed to a beam dump or a highly absorbing area of the detector box.

Wavelength calibration of BL-4 was performed using NIST Standard Reference Material 2034 of holmium-oxide solution from 240 nm to 300 nm [5]. Figure 1 shows the measured absorption peaks using the BL-4 set-up. The wavelength uncertainty from this calibration and the zeroth-order beam position is 0.1 nm.

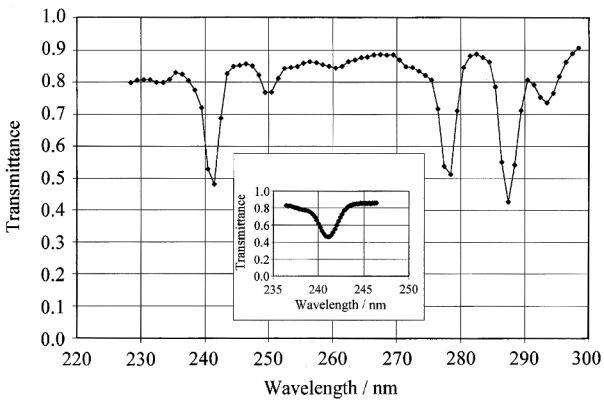

Figure 1. Wavelength calibration of BL-4 monochromator with absorption peaks of holmium-oxide solution. The inset shows a finer wavelength scan around 240 nm.

3. Transmittance measurements of CaF_2

The transmittance measurements of CaF_2 samples were performed by placing the samples on the in-vacuum translation stages and irradiating the detector mounted behind the samples by the monochromatized radiation. The translation stages moved each sample in and out of the beam. The baseline measurements (measurements with no sample in the incident beam) were performed before and after measurements with each sample in the beam path, in order to ensure repeatability. Typical wavelength scans were divided into two regions, 120 nm to 210 nm and 200 nm to 300 nm. For the 200 nm to 300 nm wavelength range, a fused-silica window was inserted in the beam path to reduce higher-order stray radiation. The estimated spectral transmittance measurement relative standard uncertainty from 140 nm to 300 nm was less than 5×10^{-3}.

At shorter wavelengths, the cleanliness of the sample has a major effect on the transmittance of the CaF_2 windows. This is demonstrated in Figure 2, where the measured spectral transmittance is shown for an uncleaned sample, a sample cleaned with acetone, and a sample cleaned with an oxygen-plasma cleaner. The highest transmittance we found was for the sample cleaned with oxygen-plasma. Work is under way at the NIST to study the effects of other cleaning procedures and of the environment on window transmittance.

The effect of bulk absorption was studied using two CaF_2 samples of different thicknesses. The samples

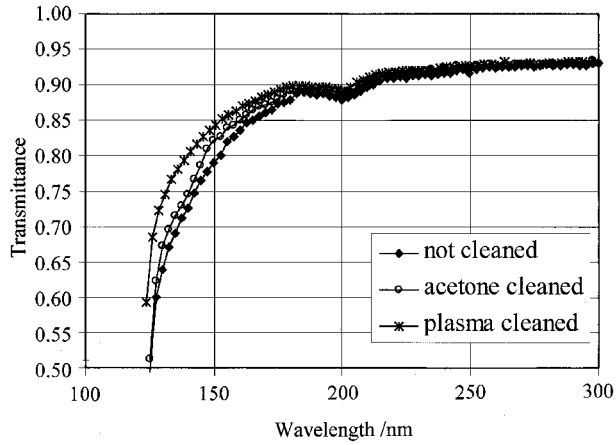

Figure 2. Measured spectral transmittance of CaF_2 with an uncleaned sample, sample cleaned with acetone, and sample cleaned with an oxygen-plasma cleaner.

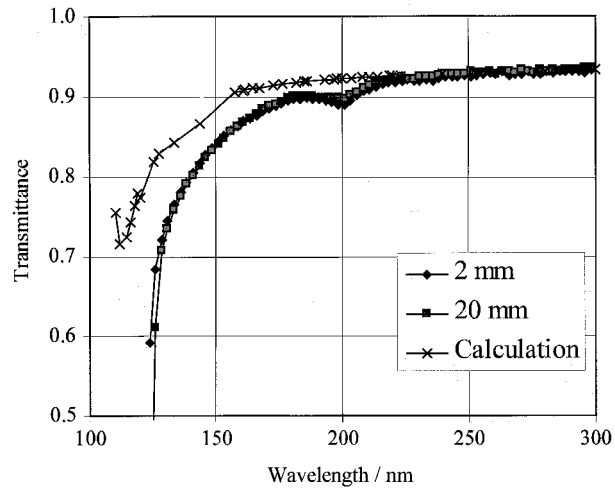

Figure 3. Measured spectral transmittance of two CaF_2 samples with thicknesses of 2 mm and 20 mm. Both samples were cleaned with an oxygen-plasma cleaner. The calculated transmittance based on the published index of refraction data for CaF_2 [5] is also shown.

were both cleaned with an oxygen-plasma cleaner before they were mounted in the detector box. Figure 3 shows the spectral transmittance of the 2 mm and 20 mm thick samples. The transmittances of both samples are very close to each other for wavelengths longer than 140 nm, indicating very small bulk absorption or imaginary part of the refraction index. Also shown in Figure 3 is the calculated transmittance of CaF_2 based on the published values of its refraction index [6]. It clearly shows up to a few percent of lower measured transmittance for wavelengths shorter than 170 nm.

As bulk absorption cannot lead to such a significant decrease in transmittance, surface effects may be responsible. Two mechanisms could cause lowered transmittance: surface scattering and surface absorption by adsorbate, impurities, or lattice defects. We have investigated surface scattering using a NIST facility for

scattering characterization to determine the role it plays in decreased transmittance at shorter wavelengths.

For BL-4, to ensure that the transmittance measurement is not affected by small-angle scattering from surfaces, the transmittance measurement was repeated with an aperture installed immediately in front of the 1 cm by 1 cm photodiode. The diameter of the aperture was 3 mm so that the aperture could not clip the 2 mm by 2 mm beam. Figure 4 shows the small difference in transmittance with and without the use of the aperture.

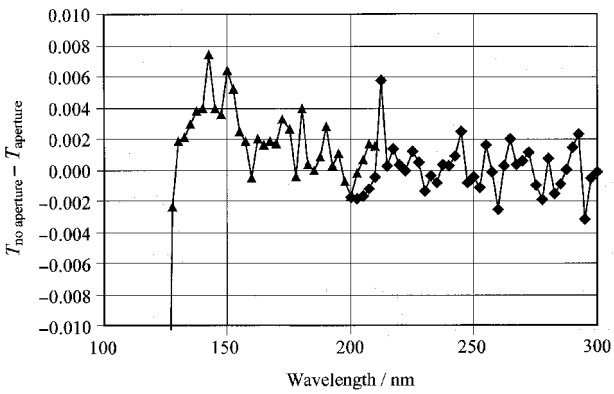

Figure 4. Changes in transmittance of a CaF_2 sample measured with and without a 3 mm diameter aperture mounted in front of the photodiode. Note that for wavelengths longer than 220 nm (◆), a quartz filter was used to eliminate higher orders.

4. Surface-scattering measurements

The light scattered by a sample can be characterized by a bidirectional scattering distribution function (BSDF) [7], defined by

$$f_s(\theta_i, \theta_s) = \frac{\partial \Phi_s}{\partial \Omega \Phi_i \cos \theta_s},$$

where θ_i is the incident angle, θ_s the scattering angle, $\partial \Phi_s / \partial \Omega$ the differential scattered power per unit solid angle and Φ_i the incident power. In general the BSDF is also a function of incident polarization and wavelength. A goniometric optical-scatter instrument at the NIST is equipped to measure the BSDF over a very wide dynamic range for fixed laser wavelengths [8]. Figure 5 outlines the optical geometry for measurements described in this paper. Light from a He-Cd laser of wavelength $\lambda = 325$ nm is incident along the surface normal of the 2 mm thick sample. The detector, having a known solid angle of collection, rotates about the front surface of the sample at a fixed distance and records the signal, as a function of the angle θ, measured with respect to the incident laser beam. The measurement was carried out for both horizontal (in the plane of the figure) polarization and vertical (out of the plane of the figure) polarization. Owing to the presence of the sample holder and the finite size of the detector, not all scattering angles can be recorded.

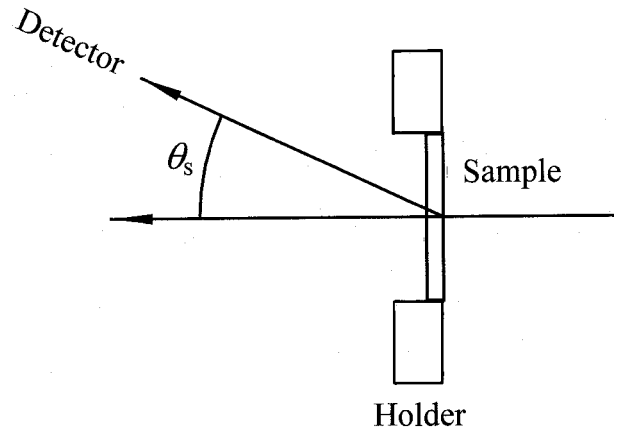

Figure 5. Geometry of the optical scattering measurements.

Figure 6 shows the resulting measured BSDF of the 2 mm CaF_2 sample. The BSDF is highly peaked near angles $\theta = 0°$ and $\theta = 180°$, corresponding to the transmitted laser beam and the specularly reflected beam, respectively. The difference between the two linear polarization states is most evident away from these angles. An estimate of the total scattered light can be obtained by integrating the BSDF:

$$R = \int_0^{\pi} f_s \cos \theta_s 2\pi \sin \theta_s \, d\theta_s.$$

Integration of this function is, of course, limited owing to the limited scattering angles accessible to the instrument. Over the finite angles covered by the measurement, the integrated scatter was found to be approximately $R = 2 \times 10^{-4}$.

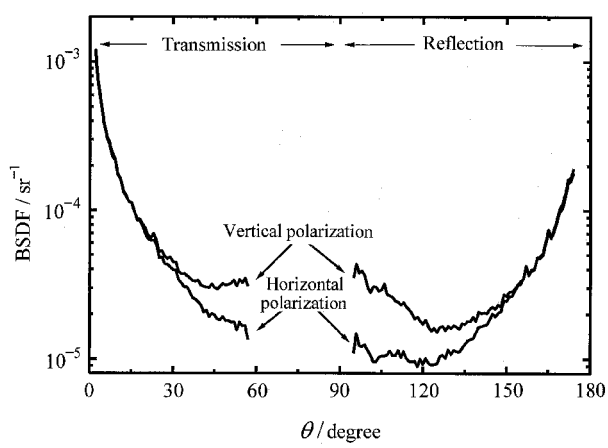

Figure 6. Measured bidirectional scattering distribution function (BSDF) at both transmitted and reflected angles of the 2 mm CaF_2 sample at a wavelength of 325 nm.

As the measurement was carried out for a wavelength much longer than that of interest, some estimated extrapolation is necessary. For scattering resulting from roughness, the total integrated scatter is proportional to $(\sigma/\lambda)^2$, where σ is the root-mean-square roughness of the surface [8]. However, the definition of

σ depends on the wavelength and details of the power spectrum of the surface roughness. For integrations over only large scattering angles, however, the integrated scatter is likely to follow $1/\lambda^4$. In this case, the fraction of scattered light at $\lambda = 140$ nm may be as much as 0.006, which is still less than the unexplained losses occurring in the transmission measurement. As an aside, this estimate does not include scattering that is trapped in the sample due to total internal reflection. Accounting for this light might increase our estimate by as much as a factor of 2. Future measurements will use wavelengths closer to those of interest.

5. Conclusions

Using the BL-4 facility at the newly upgraded SURF III, we have demonstrated accurate measurements of transmittance in the UV. We found that the transmittance of CaF_2 for wavelengths less than 200 nm depends critically on the surface-cleaning procedure. For wavelengths beyond 140 nm, there is negligible bulk absorption compared with surface absorption. The study of light scattering from surfaces shows less than 1% of light-scattering loss. This indicates that the small percentage light loss arises from other surface effects such as absorption by surface layers. We are continuing to study the effects of surface condition on the transmittance of CaF_2. This work will benefit DUV lithography in optical design by providing accurate transmittance data. We also intend to characterize other materials, such as barium fluoride and fluorine-doped fused silica, which are also considered as potential materials for use in photolithography projection-lens design.

Note. Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

References

1. Rabus H., Persch V., Ulm G., *Appl. Opt.*, 1997, **36**, 5421-5440.
2. Arp U., Friedman R., Furst M. L., Makar S., Shaw P.-S., *Metrologia*, 2000, **37**, 357-360.
3. Shaw P.-S., Lykke K. R., Gupta R., O'Brian T. R., Arp U., White H. H., Lucatorto T. B., Dehmer J. L., Parr A. C., *Metrologia,* 1998, **35**, 301-306.
4. Shaw P.-S., Lykke K. R., Gupta R., O'Brian T. R., Arp U., White H. H., Lucatorto T. B., Dehmer J. L., Parr A. C., *Appl. Opt.*, 1999, **38**, 18-28.
5. Weidner V. R., Mavrodineanu R., Mielenz K. D., Velapoldi R. A., Eckerle K. L., Adams B., Natl. Bur. Stand. Spec. Publ. 260-102, 1986.
6. Bezuidenhout D. F., In *Handbook of Optical Constants of Solids II* (Edited by E. D. Palik), San Diego, Academic Press, 1991.
7. Stover J. C., *Optical Scattering: Measurement and Analysis*, Bellingham, USA, SPIE Optical Engineering Press, 1995.
8. Germer T. A., Asmail C. C., *Rev. Sci. Instrum.*, 1999, **70**, 3688-3695.